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WET AND DRY STRENGTH AND LIQUID REPELLANCY OF FIBROUS MATERIAL

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U.S. Cl. 8—115.6 2 Claims

ABSTRACT OF THE DISCLOSURE

It has recently been found that fibrous materials such as water laid unsized paper (waterleaf paper) has increased wet and dry strength after being treated with amine oxide solvents or swelling agents such as N-methylmorpholine-N-oxide. The treated material retains its wettability, which may be a disadvantage, but most waterproofing materials interfere with the action of the amine oxides if applied first or result in excessive wetting of the sheet if applied later. The present process provides liquid repellancy by the use of a ketene, such as an alkylketene dimer, which does not interfere with effectiveness of the amine oxide, nor does the latter interfere with the effectiveness of the ketene.

Related applications are Ser. Nos. 576,810, now U.S. Patent 3,447,939, and 576,902, both filed Sept. 2, 1966.

This invention relates to a process for improving the wet and dry strength, as well as the liquid or water repellancy and resistance to liquid penetration, of fibrous materials by treating them with certain amine oxides and ketenes or ketene dimers.

Fibrous materials such as papers, felts, and fabrics made from fibers are widely used, especially in such areas as packaging, clothing, and supports for photographic emulsions where strength is required, both when the materials are dry and when they are wet. It is beneficial to strengthen these materials by a quick, simple, and inexpensive process which does not unduly modify the normal desirable characteristics of these materials. This process should result in no degradation of the material, impart no color to it, and leave no potentially dangerous or unpleasant residue in the material. The strength imparted to the materials should be permanent or long-lasting and should not be affected by washing the material with water. These objectives are fulfilled when the fibrous materials are strengthened with certain amine oxides.

When treated solely with amine oxides, such fibrous materials retain their wettability by water and other liquids, as evidenced by rapid penetration by aqueous liquids. This property is a disadvantage as to a number of uses for the fibrous products.

One procedure which was considered as a possible way to overcome this disadvantage is to size the fibrous materials, or the fibers from which they are made, with known materials to provide liquid repellancy and resistance to liquid penetration prior to treatment with the amine oxides. Such a procedure is not satisfactory for the reason that the usual sizes interfere with the effectiveness of the amine oxide treatment. Similarly, if the amine oxide treated fibrous material is dried and subsequently coated or treated with water solutions or suspensions, excessive wetting of the material may result. It has been found, according to the present invention, that the objective of retaining the benefits of the amine oxide treatment while obtaining a fibrous material which has liquid or water repellancy is achieved by also treating the fibrous material with certain ketenes or ketene dimers.

It is an object of this invention to provide a process for improving the wet and dry strength, and the resistance to wetting, of fibrous materials.

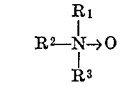
Another object of the invention is to provide fibrous structures of polymeric fibers such as thread, yarn and woven and non-woven fabrics, webs, or sheets, having the fibers thereof fused together at points of contact, and with the reaction product of a ketene or ketene dimer and said polymer being present at the surfaces of said fibers.

Still another object is the provision of a sizing composition comprising said amine oxide and said ketene dimer.

Still further objects will become apparent from the following specification and claims.

According to this invention, it has been found that a fibrous material strengthened by imbibing an amine oxide into the fibrous materal, and which is then exposed to a temperature at which the amine oxide will swell the fibers, may be further improved without interferring with the effectiveness of the amine oxide treatment, by contacting it with a ketene or a ketene dimer immediately prior or subsequent to, or at the same time as the amine oxide is imbibed.

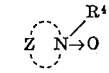
The class of amine oxides useful for strengthening fibrous materials has the general formula:



wherein each of R^1, R^2, and R^3 represents a member selected from the group consisting of monovalent alkyl, cycloalkyl, aralkyl and heterocyclic radicals, and heterocyclic rings comprising two of said members and the N-atom of the formula, with or without other atoms such as oxygen in the ring, with up to about 20 carbon atoms.

Example of alkyl groups are ethyl, octyl, and octadecyl. Cyclopentyl, cyclohexyl, cyclooctyl, and cyclododecyl are representative cycloalkyl radicals. As an aralkyl radical, benzyl is useful. The heterocyclics are represented by compounds having a total of 5 or 6 atoms in the ring, one of which is nitrogen and the other being carbon, suitably with one other atom. Examples are morpholinyl, piperidinyl, azacyclohexanyl, and pyrrolidinyl radicals.

A subclass of amine oxides, within the above formula, especially preferred for the invention, are N-alkyl or other cyclic amine oxides having the formula:



wherein Z represents the atoms to complete a saturated heterocyclic ring, and R^4 is alkyl such as methyl, ethyl, or butyl, or is an —N= or a —CH= grouping as will be illustrated below. Some preferred members within this last formula include N-methylmorpholine-N-oxide, N-methylpiperidine-N-oxide, N-methylpyrrolidone-N-oxide, N-methylazacycloheptane-N-oxide, nicotine-1-oxide, and the like. A typical example of a useful amine oxide within the first formula above is triethyl amine-N-oxide. Preferably R^4 has less than 5 carbon atoms.

The amine oxide may be imbibed into a fibrous material directly in liquid form, or it may be imbibed in solution, that is, dissolved in a liquid solvent. When solvents are used, one may use a volatile solvent which is easily removed by evaporation, or one may use a liquid solvent which will not evaporate. In the latter case, the solvent must be one that does not interfere with the strengthening action of the amine oxide.

While the amine oxide is in contact with the fibrous material to be treated, it is necessary to attain a temperature sufficiently high to let the amine oxide act as a solvent or swelling agent on the fibers. This temperature will vary, depending on the particular amine oxide, particular fiber composition, etc. In cases where the amine oxide is imbibed pure or with a solvent that evaporates, the melting point of the amine oxide is the minimum required temperature. When a solvent not removed by evaporation is used, the minimum temperature is simply the temperature required for the solution to cause the fibers to swell or begin to dissolve and will depend on the particular constituents of the solution and their concentrations.

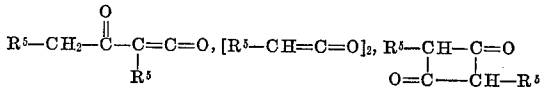
Suitable volatile solvents for imbibing the amine oxides into the fibers include water, methanol, acetonitrile, and the like. Useful solvents that are not removed by evaporation include dimethylsulfoxide, N-methylpyrrolidone, sulfolane, and the like.

After the amine oxide has acted on the fibrous material to effect hardening, it must be removed and a convenient way to do this is by washing with water or other selective solvents for the amine oxide. If not removed, the solvent action of the amine oxide in the presence of moisture will result in distortion of the fiber.

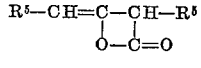
The ketenes useful in accordance with the invention may be represented by the empirical formula:

$$R^5—CH=C=O$$

wherein R^5 is a hydrocarbyl radical containing from 6 to about 20 carbon atoms, such as a straight chain or branched chain alkyl group having from about 6 to about 20 carbon atoms, examples being octyl, hexadecyl and octadecyl or is an aryl, alkaryl, or aralkyl radical such as phenyl, benzyl, or β-naphthyl, or is a cycloalkyl radical such as cyclohexyl or cyclooctyl, all as described in U.S. Patent No. 2,785,067, for example. In practice the dimer is used; it may be represented by any of the following formulate, all appearing in the literature.



and



The radicals R^5 are as described above, and in the dimer they may be the same or different hydrocarbyl radicals. A typical commercial product, which is a higher alkylketene dimer, is "Aquapel," a trademark of Hercules Powder Company. (See Hercules U.S. Patents 2,627,477; 2,762,270; and 2,785,067.)

The term "fibrous material" as used in describing the invention is applied in a broad sense to comprise any woven or nonwoven fabric containing a substantial proportion of fibers that are soluble or swellable in the amine oxide, including natural cellulosic fibers such as wood pulp, cotton, linen and the like, animal fibers such as wool, fur and the like, and synthetic fibers such as nylon, rayon, polyester fibers, etc. and mixtures of such fibers. These fibers may be separate, as in cotton or wool fibers, although they are preferably aggregated, as in papers of various kinds, felted and nonwoven fabrics and the like, or woven fabrics. A particularly preferred embodiment of the invention is the strengthening and providing liquid repellancy in papers comprising cellulosic fibers.

A possible mechanism by which the amine oxides strengthen fibrous materials can be explained by reference to cellulosic paper as an example. In strengthening paper, apparently the amine oxide partially dissolves or swells surface areas of the individual fibers of cellulose which make up the paper causing them to melt or fuse together forming a strong fiber lattice. Before treatment with the amine oxide, the paper consists of fibers which are held together mainly by interfiber friction. After treatment, the fibers are actually physically locked together. This mechanism of the strengthening process has been observed in photomicrographs of a cellulosic paper monolayer made before, during and after treatment with the amine oxides. It also appears that during treatment, loose fines in the paper are melted and fused into the cellulose fibers, becoming an integral part of the paper, thus reducing the dusting characteristics of the paper. By the same mechanism scaling is reduced in scaly fibers such as wool. In strengthening woven fabrics, the amine oxides function by the same mechanism to fuse the warp threads to the woof threads, as well as to strengthen the individual threads by fusing the fibers in the thread, resulting in a stronger physical connection of the fibers and threads than by mere interfiber friction.

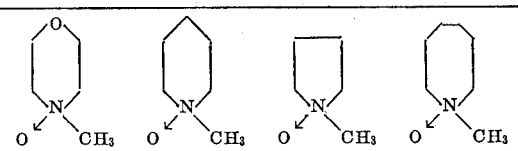
The hydrocarbylketene dimer is, on the other hand, believed to react with the fibrous material, such as cellulose (e.g., wood, linen, or cotton fibers in paper). It is preferably imbided in the fibrous material immediately before, immediately after, or simultaneosuly with the amine oxide. An important feature of one aspect of the invention is that, although the hydrocarbylketene dimer is physically present or "in place" in the fibrous material, it is maintained under conditions such that it does not react with the fibers prior to the time the swelling or dissolving effect of the amine oxide is exerted. This is possible because the alkyl ketene reacts with the fibrous material most readily at a temperature of above ordinary atmospheric temperature such as from 40° to 150° C., and the reaction requires a finite period of time. By proceeding in this way, the alkyl ketene dimer does not interfere with the swelling or dissolving effect of the amine oxide, the cellulose or other polymer continues to be reactive with the alkyl ketene compound, and the amine oxide does not destroy the effectiveness of the ketene dimer.

The amine oxide may be removed from the fibrous material before or after saturation with the ketene dimer, as by vaporization or selective solvent extraction. The quantity of amine oxide utilized and the time and temperature of exposure of the fibrous material thereto are such that the fiber structure is preserved, the surface thereof being swollen or dissolved. Where the amine oxide is a good solvent for the fibrous material, the latter may be immersed in a liquified or heated solution of the amine oxide, and immediately washed and dried. If the amine oxide is a swelling agent, the impregnated fabric usually must be heated, for example, to a temperature between about 50° C. and about 150° C.

The quantity of ketene dimer is conveniently defined on the basis of the concentration of the solution used to treat the fibrous material. Useful concentrations, for example in water, are from about 0.01% to about 2% by weight, the maximum concentration preferably being about 1%. Higher concentrations may be used, but are not preferred for reasons of economy. The preferred concentration is from about 0.1% to about 0.5%.

As illustrative of the useful fibrous materials and amine oxides which are solvents therefor, the following table is offered. It will be apparent that any fibrous material for which the amine oxide is a solvent or swelling agent, and which contains —OH groups or reactive hydrogen which will react with the ketene, is useful. For example rayon, nylon, and polyesters have been reacted with ketene dimers (see U.S. Patent 2,791,484, British Patent 815,843, and Russian Patent 170,611; 63 Ch. Abstr. 10112).

TABLE I.—SOLUBILITY OF VARIOUS NATURAL AND SYNTHETIC COMPOUNDS



A B C D

Polymer	Weight of Polymer (g.)	Solvent	Weight of Solvent (g.)	Solution Temperature (° C.)
Wool	0.5	A	5	150
	0.2	D	5	125
Silk	0.1	A	5	120
	0.2	D	5	140
Nylon	0.1	A	5	160
	0.2	D	5	130
Hair (human)	0.1	A	5	150
	0.25	D	5	150
Feathers	0.2	A	5	150
	0.2	D	5	145
	0.5	A	5	130
Poly(vinyl alcohol)	0.5	B	5	120
	0.5	C	5	120
Poly(ethylene oxide)	5.0	A	5	100
Casein	0.2	A	5	120
Zein (corn)	0.2	A	5	130
Poly(vinyl acetate)	0.2	A	5	120
Carboxymethyl hydroxyethyl cellulose.	0.2	A	5	130
Cellulose diacetate	0.1	A	5	130
Cellulose monoacetate	0.5	A	5	110
Gelatin	0.3	A	5	110
Copoly (vinyloxymethyl-morpholinium PTS) (vinyl acetate).	0.5	A	5	140
Cellulose acetate butyrate.	0.1	C	5	120
Polyethylene terephthalate.	0.5	A	5	160
Poly(acrylonitrile)	0.1	A	5	160
Polyethylene	1.0	C	5	110
	0.3	A	5	90
Cellulose	0.15	B	5	100
	0.15	C	5	100
	0.25	D	5	100

The following table shows that some of the amine oxides, closely related to those which are solvents for cellulose, are on the other hand swelling agents. Generally, those which are swelling agents require more severe conditions (e.g. higher temperatures) for best results.

TABLE II.—COMPARATIVE SOLUBILITY OF CELLULOSE IN VARIOUS TERTIARY AMINE OXIDES

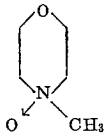
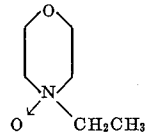
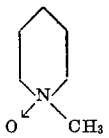
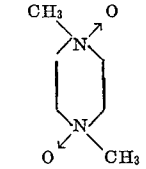
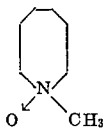
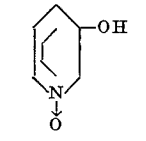
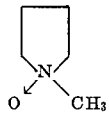
Solvents for Cellulose, Cyclic Amine Oxides of the Invention	Swelling Agents for Cellulose, Closely Related Amine Oxides
 N-methylmorpholine-N-oxide	 N-ethylmorpholine-N-oxide
 N-methylpiperidine-N-oxide	 N,N'-dimethylpiperazine-N,N'-dioxide
 N-methylazacycloheptane-N-oxide	 Quinuclidinol-N-oxide

TABLE II—Continued

Solvents for Cellulose, Cyclic Amine Oxides of the Invention	Swelling Agents for Cellulose, Closely Related Amine Oxides
 N-methylpyrrolidine-N-oxide	 1,4-diazabicyclo[2.2.2]octane-1,4-dioxide

Another example of a swelling agent is $(C_2H_5)_3N\rightarrow O$ (triethylamine oxide).

Where the fibrous structure is paper it may contain inert fillers or pigments such as silicates, carbonates, titanium dioxide and the like.

The examples given below are representative of useful ways of carrying out the invention, but it is not intended that the invention be limited thereto.

EXAMPLE 1

For the purpose of comparison, a 10 lb./1000 sq. ft. high α-cellulose waterleaf paper was saturated with a 25% solution of N-methyl morpholine N-oxide in water. After drying at 210–240° F. until bone dry (less than 1% H_2O) the sheet was washed in running water to selectively remove the amine oxide and then redried. The physical properties appear in column 1 of Table III.

The same base sheet was saturated with a 1% solution of "Aquapel 380" (alkylketene dimer; see Hercules patents noted above) in water, dried to about 5% moisture at about 240° F., saturated with a 25% solution of the same amine oxide as used above in water, dried at 210–240° F., washed in water and redried. The results (column 2, Table III) show that the physical properties (tear, Mullen, wet tensile, and fold) remain essentially unchanged, but the penetration resistance is greatly improved.

EXAMPLE 2

The same base sheet as in Example 1 was saturated with a 25% solution of the same amine oxide in water, dried at about 240° F., to 5% moisture, saturated with a 1% water solution of "Aquapel," dried until bone dry at 210–240° F., washed in water, and redried. The results (column 3, Table III) are comparable to Example 1.

EXAMPLE 3

The same base sheet as in Example 1 and 2 was saturated with a 25% solution of the same amine oxide plus 1% "Aquapel 380" in water, dried until bone dry, washed in water and redried. The results were comparable to those of Examples 1 and 2 (column 4 of Table III).

While water was used as the washing liquid, methanol or other amine oxide solvent may be used. Similarly, the amine oxide may be applied without solvent, or with another solvent therefor.

TABLE III

	Example			
	1		2	3
Column	1	2	3	4
Weight (lb./1,000 sq. ft.)	10¼	10¼	10¼	10¼
Thickness (mils)	2.7	2.7	2.7	2.7
Elmendorf Tear:				
L	24	25	24	24
C	24	24	24	23
Mullen (p.s.i.)	23	23	22	24
Wet Tensile	14	16	15	15
Penetration, sec*	1	44	41	38
2 min. Expan. (H_2O), percent	1.45	1.65	1.60	1.55
M.I.T. Fold:				
L	285	238	239	224
C	179	177	241	208

* Sodium carbonate solution (50/50) in Valley Penetration Testing Instrument.

While the foregoing examples show the improvement of preformed sheets of fibrous material by the invention, other procedures are useful. One location where the amine oxide may be applied is while the web is on the forming wire, or by tub sizing in the drying end of the paper machine, by known methods. The reaction of the ketene dimer takes place either over a period of several days at room temperature, or in a few minutes at elevated temperatures, so it is necessary to apply the amine oxide prior to substantial heating of the web containing the ketene dimer. It is preferred, however, that the ketene compound be applied to a preformed woven or felted fibrous web material. Other materials which react with cellulose, such as the isocyanate compounds of U.S. Patent No. 3,050,437, are useful with or in place of the ketenes.

Although the invention has been described in considerable detail with particular reference to certain preferred embodiments thereof, variations and modifications can be effected within the spirit and scope of the invention as described hereinbefore and as defined in the appended claims.

I claim:

1. A method of improving the wet strength, dry strength, and resistance to penetration by liquids of unsized paper, comprising imbibing the paper with an amine oxide capable of swelling the paper fibers and a ketene dimer paper sizing agent, heating the paper to swell the fibers and removing the amine oxide from the paper by vaporization, washing or solvent extraction.

2. The method of claim **1** wherein the ketene dimer is an alkyl ketene dimer the alkyl groups of which contain about 6 to 20 carbon and the amine oxide is N-methylmorpholine-N-oxide.

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